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Mg Isotope Interlaboratory Comparison of Reference Materials from Earth-Surface Low-Temperature Environments

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To enable quality control of measurement procedures for determinations of Mg isotope amount ratios, expressed as $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values, in Earth-surface studies, the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of eight reference materials (RMs) were determined by interlaboratory comparison between five laboratories and considering published data, if available. These matrix RMs, including river water SLRS-5, spring water NIST SRM 1640a, Dead Sea brine DSW-1, dolomites JDo-1 and BCS-CRM 512, limestone BCS-CRM 513, soil NIST SRM 2709a and vegetation NIST SRM 1515, are representative of a wide range of Earth-surface materials from low-temperature environments. The interlaboratory variability, $2s$ (twice the standard deviation), of all eight RMs ranges from 0.05 to 0.17‰ in $\delta^{26}\text{Mg}$. Thus, it is suggested that all these materials are suitable for validation of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ determinations in Earth-surface geochemical studies.

Keywords: Earth-surface, interlaboratory comparison, low-temperature, Mg isotopes, reference materials.

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Magnesium is a major element of the silicate Earth and vital in biogeochemical cycling. It has three stable isotopes: ^{24}Mg (78.99%), ^{25}Mg (10.00%) and ^{26}Mg (11.01%). Analytical improvements over the past decades have made the differentiation between the Mg isotope amount ratios (expressed as $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ relative to the international δ -zero reference material DSM3; Equation (1); Galy *et al.* 2003, IUPAC, see Brand *et al.* 2014) of terrestrial materials possible and enable today's rapid increase in the use of Mg isotopes as a powerful tool in investigations of Earth's biogeochemistry (e.g., Young and Galy 2004, Teng 2017). Yet, determinations of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of natural samples are challenging, due to the significant risk of bias introduced during Mg purification, the large instrumental mass bias and the sensitivity of the

calibrator-sample bracketing (standard-sample-bracketing, SSB) measurements to matrix effects (e.g., Young and Galy 2004, An and Huang 2014, Teng 2017). Hence, processing well-characterised reference materials (RMs), similar in matrix to the samples, is required to validate the results. While $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of silicate rock RMs are available for high-temperature systems (Teng *et al.* 2015), Mg isotope data of RMs representative of samples with complex matrices from Earth-surface low-temperature environments are scarce (Bolou-Bi *et al.* 2009, Foster *et al.* 2010, An and Huang 2014, Teng 2017). To assess systematic errors and achieve comparability of Mg isotope data between different laboratories concerning Earth-surface low-temperature systems, well-characterised matrix RMs need to be established.

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$\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values are being used as a biogeochemical tool to study many different processes in low-temperature environments, for example in marine environments and marine sediments and rocks (e.g., Ling *et al.* 2011, Wombacher *et al.* 2011, Pogge von Strandmann *et al.* 2014, Higgins and Schrag 2015), evaporitic environments (e.g., Geske *et al.* 2015, Shalev *et al.* 2017), soils and vegetation (e.g., Tipper *et al.* 2010, Opfergelt *et al.* 2012, Pogge von Strandmann *et al.* 2012, Ma *et al.* 2015, Uhlig *et al.* 2017) and groundwater, spring water and rivers (e.g., Tipper *et al.* 2006a, b, Brenot *et al.* 2008, Pogge von Strandmann *et al.* 2008, Chapela Lara *et al.* 2017). The most fractionated materials on Earth are found in low-temperature environments, with the lowest $\delta^{26}\text{Mg}$ values found in carbonates ($\delta^{26}\text{Mg}$ of -5.6‰ , Wombacher *et al.* 2011) and the highest in weathered residual silicates ($\delta^{26}\text{Mg}$ of $+1.8\text{‰}$, Liu *et al.* 2014) and evaporites ($\delta^{26}\text{Mg}$ of $+1.4\text{‰}$, Permian camallite, Shalev *et al.* 2017). However, the only natural Earth-surface RM which is well characterised to date is seawater ($\delta^{26}\text{Mg}$ of $-0.83 \pm 0.09\text{‰}$; 2s; $N = 90$; Foster *et al.* 2010, Ling *et al.* 2011 and references therein). Published $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ data of Earth-surface materials from more than two laboratories ($N > 2$) are also available for limestone Cal-S ($-4.38 \pm 0.09\text{‰}$, 2s, $N = 3$; Wombacher *et al.* 2006, Bolou-Bi *et al.* 2009), shale SCo-1 ($-0.89 \pm 0.08\text{‰}$, 2s, $N = 3$), aragonite JCp-1 ($-1.96 \pm 0.05\text{‰}$, 2s, $N = 4$) and dolomite JDo-1 ($-2.37 \pm 0.04\text{‰}$, 2s, $N = 5$; Teng 2017 and references therein). Here, N is used to denote the number of full-procedure replicates, that is independent sample dissolution and Mg purification, while n is used to denote the number of repeated measurements of the purified Mg sample solutions by MC-ICP-MS. 2s is twice the standard deviation on N or n values.

In this study, the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of eight RMs (Table 1), representative for their respective Earth-surface environments, were estimated by interlaboratory comparison, conducted in five laboratories. The participating laboratories utilised different sample preparation methods, that is different analyte-matrix separation procedures, and MC-ICP-mass spectrometers from various manufacturers with different sample introduction systems (Table 2). This approach is suitable to test the applicability of these different measurement methods with respect to the varying chemical and physical material properties and to identify potential bias originating from differences in sample preparation and instrument set-up. Whereas measurement results from a single laboratory might produce very precise $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for any material never analysed before, there is still the potential risk that the data are affected by undetected bias. We suggest that our interlaboratory

comparison study provides a robust and practicable approach to provide the geo-analytical community with fit-for-purpose $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for matrix RMs with confidence intervals constrained by the currently attainable level of measurement precision. Materials of this study included solids (carbonates, soil and organic material) and liquids (river water, spring water and brine) thereby representing most of the material types from Earth-surface low-temperature environments studied to date. Most selected RMs are provided by reference material producers and are widely available to the community. Also, certified mass fractions data are available for most materials studied in this work (Table 1). Based on the results of this study and published values, where available, recommended $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values are proposed. These can be used as quality control RMs in laboratories analysing Earth-surface materials to verify their measurement methods.

Methods

Investigated materials

The investigated materials include dolomites JDo-1 and BCS-CRM 512, limestone BCS-CRM 513, NIST SRM 2709a soil, NIST SRM 1515 apple leaves, IAPSO Atlantic seawater, SLRS-5 river water, NIST SRM 1640a spring water and DSW-1 Dead Sea brine. Solid samples are powdered and require complete dissolution prior to the column chemistry. The published chemical compositions of the investigated materials are described in Table 1. $\sum c(\text{Matrix cations})/c(\text{Mg})$ molar ratios (i.e., the molar ratios of the sum of Na, K, Ca, Si, Al, Ti, Fe and Mn relative to Mg) of the RMs vary significantly: Na/Mg ratios range between 0.0 (carbonates) and 8.8 (seawater), Ca/Mg ratios range between 0.2 (seawater) and 220 (BCS-CRM 513 limestone) and K/Mg ratios range between 0.0 (JDo-1 and BCS-CRM 512 dolomites) and 3.7 (NIST SRM 1515 apple leaves). The soil (NIST SRM 2709a), spring water (NIST SRM 1640a) and limestone (BCS-CRM 513) have the most complex matrices with significant Si/Mg ratios (18, 3.3 and 0.8, respectively), Al/Mg ratios (4.6, 0.04 and 0.45, respectively), Fe/Mg ratios (1.0, 0.02 and 0.08, respectively) and Ti/Mg ratio (0.12 in the soil NIST SRM 2709a).

Measurement procedures

The eight RMs, IAPSO Atlantic seawater and Cambridge-1 were analysed for $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values in the laboratories of the University of Bristol (BIG) and University of London (UCL), UK (BIG LOGIC); The Geological Survey of Israel (GSI), Jerusalem, Israel; the Helmholtz Laboratory for the Geochemistry of the Earth Surface (HELGES) at GFZ

Table 1.
Reference materials studied and their chemical composition

CRM	Producer	Data source	g/100 g													mol mol ⁻¹ Σ c(matrix-cations)/c(Mg) ^a	
			SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ (total)	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	BaO	S		
Solids																	
	GSI	b	0.216	0.001	0.017	0.0208	0.007	18.47	33.96	0.013	0.002	0.034	46.5			1.3	
	BAS	b	0.379	0.002	0.055	0.03	0.004	21.59	30.61	< 0.15	< 0.01	< 0.001	46.66	< 0.02	< 0.0085	1.0	
	BAS	b	0.228	< 0.007	0.108	0.0275	0.01	0.182	55.59	< 0.05	0.015	< 0.01	43.71	< 0.02	0.01	220	
	NIST	b	64.81	0.56	13.92	4.80	0.068	2.42	2.67	1.6	2.54	0.16				26	
μg g ⁻¹																	
Liquids			Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	N _(total)	C _(total)	Ba	S	Cl
	NIST	b	286			83	54	2710	15260	24.4	16100	1590	22500	49	1800	579	7.2
	μg ml ⁻¹																
			Si		Al	Fe	Mn	Mg	Ca	Na	K			C _(total)	Ba	S	Cl
	Univ. of Cambridge OSIL	c	10000			5.5E-5	1E-05	1290	412	10770	399			27.6	0.014	904	19354
Cambridge-1 (Mg solution) IAPSO (Atlantic seawater) SIBS-5 (river water) (CCRM) SRM 1640a (spring water)	b	0.002		0.05	0.0912	0.004	2.54	10.5	5.38	0.839				0.014			5.0
	b	5.169		0.053	0.0365	0.04	1.05	5.57	3.112	0.575				0.151			10
	mmol kg ⁻¹																
DSW-1 ^f (Dead Sea brine)	GSI	d, e	Si		Al	Fe	Mn	Mg	Ca	Na	K			C _(total)	Ba	S	Cl
			1663			391	1081	169		0.86		5294	0.9				

^a Refers to the molar ratio of the sum of Na, K, Ca, Si, Al, Ti, Fe and Mn relative to Mg. ^b Producer's certificate of analysis. ^c Summerhayes and Thorpe (1996). ^d Golan *et al.* (2016). ^e Concentrations refer to average Dead Sea composition (in 2013) and may be slightly different from DSW-1, although elemental mass ratios are similar. ^f DSW-1 can be freely obtained from the Geological Survey of Israel (GSI).

Potsdam, Germany; the Czech Geological Survey (CGS) in Prague (Czech Republic); and the GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany. The powdered or liquid RMs were split and spread among the different laboratories. Each laboratory conducted measurements, using its own previously established measurement procedure, to get completely independent results and potentially identify any method-specific bias. The different procedures for material digestion, Mg purification and instrumentation, conducted in each laboratory, are described below and summarised in Table 2. All Mg isotope ratio measurements were conducted by MC-ICP-MS using calibrator-sample bracketing (with DSM3 as the calibrator), and the calculated isotope amount ratios are reported as per mil deviation from the delta-zero reference material DSM3 in the delta notation according to Coplen (2011):

$$\delta^x\text{Mg} = \delta^{x/24}\text{Mg}_{\text{sample/DSM3}} = \left[\frac{(^x\text{Mg}/^{24}\text{Mg})_{\text{sample}}}{(^x\text{Mg}/^{24}\text{Mg})_{\text{DSM3}}} - 1 \right] \quad (1)$$

where x denotes either 26 or 25 and DSM3 is the mean value of the two bracketing calibrators measured before and after the sample, respectively. Multiplication of Equation (1) by a factor 1000 gives the per mil (‰) deviation relative to DSM3.

To validate the different measurement procedures used by the participating laboratories and to test for any potential interlaboratory bias, we adapted the following approach. During this study, Cambridge-1 and IAPSO Atlantic seawater were analysed by all participating laboratories. These results are compared with literature values (e.g., compilations in Teng 2017, An and Huang 2014, and the in GeoReM database, Jochum *et al.* 2005) in order to validate the measurement procedure of each laboratory. Thereby, the pure Mg-solution Cambridge-1 was used to evaluate the repeatability precision of the MC-ICP-MS measurements (solution not processed through columns) for each laboratory. Then, seawater was used to evaluate the intermediate precision of the entire measurement procedure for each laboratory, including sample pre-treatment, matrix separation by column chemistry and MC-ICP-MS analysis. In addition, a typical intermediate precision was estimated by each laboratory (Table 2), based on long-term (more than 1 year) repeated measurements of one or more matrix materials as detailed below (following subsections). The only case where this long-term experience with matrix material is missing is at GEOMAR, and therefore only Cambridge-1 repeatability precision was considered. These estimates are considered as a benchmark against which we can evaluate the precision obtained on the matrix

RMs investigated in this interlaboratory comparison study. Then, to provide consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for each Earth-surface reference material, the arithmetic mean of $N \geq 3$ full-procedure replicates was calculated. These comprised all data produced by the participating laboratories and – where available – literature data and are reported together with 95% confidence intervals.

Sample preparation and Mg isotope ratio measurements at UCL and Bristol (BIG LOGIC): Procedures for sample analyses are similar to those described in previous studies (Pogge von Strandmann 2008, Foster *et al.* 2010, Pogge von Strandmann *et al.* 2011, 2012). A brief description is given below.

Carbonate powders (ca. 20 mg) were dissolved in 2 mol l⁻¹ HCl. Apple leaves (NIST SRM 1515, ca 50 mg) were dissolved in repeated steps of concentrated HNO₃, heated at 130 °C and evaporated to dryness. Soil powders (ca. 10 mg) were dissolved in stages of concentrated HF-HNO₃, followed by HNO₃, and finally 6 mol l⁻¹ HCl. Water samples (ca. 0.01–0.2 ml) were simply dried down. Subsequently, the samples were dissolved in 2 mol l⁻¹ HNO₃, and a small aliquot (around 0.2–3 µg Mg) was taken for column chemistry.

Magnesium analyte-matrix separation was performed by a two-stage cation exchange chemistry, using Bio-Rad AG® 50W-X12 (200–400 mesh) resin in 2 mol l⁻¹ HNO₃, as described by Pogge von Strandmann *et al.* (2011). Soil samples were subjected to an additional column to quantitatively remove Ti (because ⁴⁸Ti²⁺ and ⁵⁰Ti²⁺ are direct interferences on ²⁴Mg⁺ and ²⁵Mg⁺). This column contained 0.25 ml of TRU-Spec™ resin, and Mg was eluted in 7 mol l⁻¹ HNO₃ (Pogge von Strandmann *et al.* 2012). The total procedural blank for Mg isotope ratio measurements by this method is ca. 0.4 ng Mg, which is insignificant compared to the amount of Mg put through chemistry (< 0.2%). Splits of the elution were collected before and after the Mg collection bracket, to ensure close to 100% Mg yield was achieved, that is < 0.1% of the processed Mg was detected in these splits.

Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-MS with a high-sensitivity 'X' Ni skimmer cone and conventional Ni sample cone interface. A purified sample solution of ca. 100 ng ml⁻¹ Mg was introduced via an Elemental Scientific Inc. Apex-Q, with a ca. 50 µl min⁻¹ uptake rate nebuliser tip, in 2% v/v HNO₃. Mg isotope ratios were measured in low mass resolution mode (see footnote in Table 2), with all intensities at m/z 24, 25 and 26 measured simultaneously in separate Faraday cups (H3, Centre, L3). Each individual

Table 2.
Summary of analytical techniques used by each laboratory

Laboratory	Test portion ^a	Dissolution method	Mg column purification	Typical column procedure blank	Instrument ^b , sample introduction system, uptake rate, acid matrix	Integration time / bracket ^c , number of brackets ^d , ²⁴ Mg signal intensity / analyte concentration Typical Mg consumption per single analysis ($n = 1$) ^e	Typical intermediate precision on $\delta^{26}\text{Mg}$; $\delta^{25}\text{Mg}$ (2s)
UCL/Bristol	10–50 mg (0.2–3 μg Mg)	Carbonates: HCl Leaves: $\text{HNO}_3 + \text{H}_2\text{O}_2$ Soil: HF/ $\text{HNO}_3 + \text{HCl}$ liquids: evaporation	2 steps: Bio-Rad AG50W-X12 resin in 2 mol l^{-1} $\text{HNO}_3 + \text{TRUSpec}$ in 7 mol l^{-1} HNO_3	< 0.4 ng Mg	Neptune (LR), Apex-Q desolvator, 50 $\mu\text{l min}^{-1}$, 2% HNO_3	20 \times 4.2 s, 1 18–20 V / 100 ng ml^{-1} Mg 7 ng Mg	$\pm 0.06\text{‰}$; $\pm 0.04\text{‰}$
GSI	100–150 mg (200–500 μg Mg)	Carbonates: HNO_3 Liquids: evaporation	1 step: Bio-Rad AG50W-X12 resin in 1.3/2.3 mol l^{-1} HCl	< 100 ng Mg	NU plasma II (MR), DSN-100 desolvator, 100 $\mu\text{l min}^{-1}$, 0.1 mol l^{-1} HNO_3	20 \times 10 s, 1 25–35 V / 2000 ng ml^{-1} Mg 670 ng Mg	$\pm 0.11\text{‰}$; $\pm 0.05\text{‰}$
GFZ	30–100 mg / in addition 1 g for NIST SRM 1515 (2.5–1.5 μg Mg)	Carbonates: HCl Leaves: $\text{HNO}_3 + \text{H}_2\text{O}_2$ Soil: HF/ $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_2$ liquids: HF + evaporation + H_2O_2	2 steps: Bio-Rad AG50W-X12 resin in 1 & 2 mol l^{-1} HNO_3 (repeated twice)	< 12 ng Mg	Neptune (MR), double pass cyclone-Scott quartz-glass spray chamber (SS), 100 $\mu\text{l min}^{-1}$, 0.3 mol l^{-1} HNO_3	20 \times 4.2 s, 1 10–15 V / 500 ng ml^{-1} Mg 70 ng Mg	$\pm 0.10\text{‰}$; $\pm 0.06\text{‰}$
CGS	50–100 mg (20–50 μg Mg)	Carbonates: HCl Leaves: $\text{HNO}_3 + \text{H}_2\text{O}_2$ Soil: HF/ HNO_3 liquids: evaporation	3 steps: Bio-Rad AG50W-X12 resin in 2.5 mol l^{-1} HCl (twice) + 0.4 mol l^{-1} HNO_3	< 2 ng Mg	Neptune (MR), cyclonic quartz-glass spray chamber, 100 $\mu\text{l min}^{-1}$, 3% v/v HNO_3	30 \times 8.4 s, 3 4–8 V / 500 ng ml^{-1} Mg 630 ng Mg	$\pm 0.13\text{‰}$; $\pm 0.09\text{‰}$
GEOMAR	Same as CGS	Same as CGS	Same as CGS	Same as CGS	AXIOM (LR), Airdus desolvator, 50 $\mu\text{l min}^{-1}$, 5% HNO_3	50 \times 2 s, 9 3.5 V / 200 ng ml^{-1} Mg 150 ng Mg	$\pm 0.08\text{‰}$; $\pm 0.06\text{‰}$

^a The test portion refers to the aliquot amount of the original sample taken for analysis. Amount of Mg processed through column purification is given in parenthesis.

^b LR and MR refers to the mass resolving power R_p , defined as $m/\Delta m = m/[m(5\%) - m(95\%)]$, where $m(5\%)$ and $m(95\%)$ are the masses at 5% and 95% peak intensity, respectively, and m is the mass of the peak. LR = low R_p (ca. > 1000), MR = medium R_p (> 6000).

^c Integration time/bracket refers to the measurement time of a sample or each one of the bracketing calibrators in a single bracket.

^d The number of brackets that were used to calculate a single δ result ($n = 1$ in Table 3).

^e Including the data acquisition time only, without take-up time, etc.

measurement consisted of twenty ratios (84 s total integration time). These conditions gave typical signals of 18–20 V per 100 ng ml⁻¹ on ²⁴Mg. The on-peak background in 2% v/v HNO₃ was repeatedly recorded during the sequence and subtracted from all calibrator and sample intensities. Each sample was analysed three or four times ($n = 3$ or $n = 4$ in Table 3) during the same session (336 s per sample), each time separated by several hours. The difference in the measured ²⁶Mg/²⁴Mg intensities ratio between bracketing DSM3 calibrators was $\leq 0.06\%$ in all analyses performed for this study.

USGS (United States Geological Survey) and GSJ (Geological Survey of Japan) silicate rock reference material measurement results by this procedure are documented by Pogge von Strandmann *et al.* (2011), other silicate rocks by Teng *et al.* (2015), IAPSO Atlantic seawater results by Foster *et al.* 2010 and carbonates by Pogge von Strandmann 2008, Kasemann *et al.* (2014) and Pogge von Strandmann *et al.* (2014). For example, measurements of the pure Mg solution Cambridge-1 (without processing through columns) gave $-2.63 \pm 0.07\%$ for $\delta^{26}\text{Mg}$ and $-1.36 \pm 0.06\%$ for $\delta^{25}\text{Mg}$ (2s, $n = 126$) and IAPSO Atlantic seawater results were $-0.82 \pm 0.06\%$ for $\delta^{26}\text{Mg}$ and $-0.43 \pm 0.04\%$ for $\delta^{25}\text{Mg}$ (2s, $n = 26$, Foster *et al.* 2010). Hence, the typical intermediate precision of this method, based on several years of repeated measurements, is estimated at $\pm 0.06\%$ (2s) on $\delta^{26}\text{Mg}$, and $\pm 0.04\%$ (2s) on $\delta^{25}\text{Mg}$. The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

Sample preparation and Mg isotope ratio measurements at GSI: Carbonate powders (ca. 100–150 mg) were dissolved in HNO₃ and evaporated to dryness. Water samples (ca. 10 µl DSW-1 and 2 ml IAPSO) were simply dried down. All samples were then redissolved in 10 ml 1.3 mol l⁻¹ HCl, and an aliquot (200–500 µg Mg) was taken for column chemistry.

Magnesium purification was performed by liquid chromatography (Galy *et al.* 2002) using Bio-Rad Econo-Pac Chromatography Columns 732-1010 with an extended reservoir, filled with ca. 18 ml of Bio-Rad AG® 50W-X12 100-200 mesh resin. The matrix was rinsed with 25 ml of 1.3 mol l⁻¹ HCl, and 20 ml of 2.3 mol l⁻¹ HCl. Mg²⁺ was then eluted with 24 ml of 2.3 mol l⁻¹ HCl. Total procedural blanks contained $< 0.5\%$ Mg of the amount of Mg processed through column chemistry. The first and the last 2 ml before and after the Mg elution were collected separately in order to verify close to 100% Mg recovery. In addition, the Mg amount in the Mg cut (Mg-COL) was compared to the amount originally loaded to the column

(Mg-ORIG). Only samples with Mg-COL/Mg-ORIG $> 95\%$ (taking into account the uncertainties of both measurements), no detectable Mg in the first and the last 2 ml before and after the Mg fraction, and molar ratio of $\sum c(\text{matrix cations})/c(\text{Mg})$ in the final Mg fraction of $< 5\%$ (after Galy *et al.* 2001 and others) were used for isotope ratio measurements. These parameters were verified for each sample separation using ICP-AES (Optima 3300, Perkin-Elmer). Once Mg was purified, the solution was fully evaporated and the chloride salts were redissolved in 0.1 mol l⁻¹ HNO₃.

Magnesium isotope ratio measurements were conducted using a Nu instruments Plasma II HR-MC-ICP-MS. The 2 µg ml⁻¹ Mg solutions (in 0.1 mol l⁻¹ HNO₃) were introduced into the mass spectrometer via a DSN-100 desolvation system (self-aspirating PFA nebuliser, uptake rate of ca. 100 µl min⁻¹) and standard Ni cones interface. The measurements were conducted using pseudo-high resolution, with a 50 µm source slit at a mass resolving power $R_p(5,95\%) = 7000$ (see footnote in Table 2). Three Faraday cup collectors were used to measure the ion beam intensities at m/z 24, 25 and 26 simultaneously. Each measurement run comprises twenty integrations of 10 s data acquisition, that is a total 200 s of data acquisition per measurement. These conditions gave sample signal intensities of 25–35 V on m/z 24. The zero reference points were reset simultaneously for all measured masses by deflecting the potential of the electrostatic analyser before measuring each block. A blank solution measured in the beginning of each measurements day produced < 5 mV on m/z 24, and therefore, the difference from the off-peak zero is considered insignificant. Each sample solution was measured by several brackets of calibrator-sample-calibrator, which were used for statistical analysis, where n is the number of brackets of each sample. Outliers were eliminated as long as their elimination reduced the 95% confidence interval ($= t \cdot \frac{s}{\sqrt{n}}$), despite the reduction of n that rises both $\frac{1}{\sqrt{n}}$ and the t -distribution value.

The $\delta^{26}\text{Mg}$ mean of pure Mg Cambridge-1 solution measured in this study is $-2.62 \pm 0.14\%$ (2s, $n = 36$, Table 3), identical within stated precisions to results reported by other laboratories (e.g., compilations by Teng 2017, An and Huang 2014, $-2.61 \pm 0.05\%$, 2s). The $\delta^{26}\text{Mg}$ value of IAPSO Atlantic seawater reference material measured in this study ($-0.84 \pm 0.09\%$, 2s, $n = 12$, Table 3) is also identical to the previously reported seawater value ($-0.83 \pm 0.09\%$, 2s, $N = 90$; Foster *et al.* 2010, Ling *et al.* 2011 and references therein). In order to further test the measurement procedure, a sample of modern Dead Sea brine (DSW-1) was purified through Mg column chemistry and this single solution was repeatedly measured over 2 years

Table 3.
 $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of the low-temperature RMs determined in the current and previous studies

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf ^a	2s	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf ^a	2s	n ^b
Internationally established RMs							
Cambridge-1 (pure Mg solution)							
Bristol/UCL ^d	-2.63	0.01	0.07	-1.36	0.00	0.05	126
CGS	-2.59	0.04	0.16	-1.34	0.03	0.11	18
GSI	-2.62	0.02	0.14	-1.35	0.01	0.07	36
GFZ	-2.61	0.01	0.07	-1.35	0.01	0.05	62
GEOMAR ^e	-2.63	0.15	0.12	-1.31	0.04	0.03	3
Arithmetic mean	-2.62	0.02	0.03	-1.34	0.02	0.04	N^c = 5
An and Huang (2014) (compilation)	-2.61		0.05				
IAPSO Atlantic seawater (OSIL)							
Bristol/UCL ^f	-0.82	0.01	0.06	-0.43	0.01	0.04	26
CGS	-0.87	0.03	0.10	-0.45	0.02	0.06	14
GSI	-0.84	0.03	0.09	-0.44	0.02	0.05	12
GFZ A	-0.81	0.03	0.12	-0.41	0.02	0.06	13
GFZ B ^{g,h}	-0.85	0.06	0.07	-0.43	0.05	0.07	4
GEOMAR	-0.81	0.05	0.04	-0.40	0.05	0.04	3
Arithmetic mean	-0.83	0.02	0.05	-0.43	0.02	0.04	N^c = 6
Ling <i>et al.</i> (2011) (compilation)	-0.83		0.09	-0.43		0.06	90
Surface water RMs							
DSW-1 (Dead Sea brine)							
CGS	-0.68	0.09	0.17	-0.34	0.05	0.10	6
GSI A	-0.67	0.02	0.11	-0.35	0.01	0.05	35
GSI B ^{g,i}	-0.51	0.03	0.07	-0.28	0.01	0.03	8
GFZ A	-0.59	0.31	0.07	-0.30	0.17	0.04	2
GFZ B ^g	-0.57	0.05	0.10	-0.30	0.03	0.06	7
GFZ C ^g	-0.53	0.05	0.12	-0.26	0.03	0.07	7
GFZ D ^g	-0.54	0.06	0.08	-0.26	0.05	0.06	4
Karasinski <i>et al.</i> (2017) ^j	-0.57	0.06	0.18				10
Arithmetic mean	-0.58	0.05	0.12	-0.30	0.03	0.07	N^c = 8
SLRS-5 (river water)							
Bristol/UCL	-1.14	0.05	0.06	-0.59	0.04	0.05	4
CGS	-1.11	0.10	0.20	-0.60	0.06	0.12	6
GFZ A ^g	-1.30	0.43	0.10	-0.72	0.31	0.07	2
GFZ B ^g	-1.31	0.05	0.09	-0.67	0.02	0.04	6
GFZ C ^g	-1.25	0.03	0.06	-0.65	0.02	0.05	6
GFZ D ^g	-1.24	0.05	0.12	-0.64	0.03	0.07	8
GFZ E ^{g,h}	-1.28	0.04	0.10	-0.67	0.03	0.07	10
GEOMAR	-1.17	0.05	0.04	-0.57	0.03	0.03	3
Arithmetic mean	-1.22	0.06	0.15	-0.64	0.04	0.10	N^c = 8
NIST SRM 1640a (spring water)							
Bristol/UCL A ^g	-0.76	0.06	0.05	-0.42	0.06	0.05	3
Bristol/UCL B ^g	-0.81	0.07	0.05	-0.44	0.05	0.04	3
CGS	-0.72	0.10	0.16	-0.35	0.04	0.07	5
GFZ A ^g	-0.75	0.14	0.03	-0.39	0.46	0.10	2
GFZ B ^g	-0.73			-0.37			1
GFZ C ^g	-0.72	0.07	0.06	-0.39	0.07	0.05	3
GFZ D ^g	-0.68	0.02	0.07	-0.35	0.01	0.03	13
GFZ E ^{g,h}	-0.73	0.05	0.03	-0.39	0.06	0.03	6
GEOMAR	-0.68	0.07	0.06	-0.31	0.04	0.03	3
Arithmetic mean	-0.73	0.03	0.08	-0.38	0.03	0.08	N^c = 9
Organic-rich solids							
NIST SRM 2709a (soil)							
Bristol/UCL	-0.20	0.02	0.02	-0.11	0.04	0.03	3
CGS	-0.11	0.07	0.17	-0.07	0.04	0.08	8
GFZ A (MW) ^g	-0.14	0.02	0.09	-0.07	0.01	0.05	19
GFZ B ^g	-0.17	0.04	0.10	-0.09	0.02	0.05	8
GFZ C ^g	-0.15	0.06	0.08	-0.08	0.04	0.05	4

Table 3 (continued).

$\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of the low-temperature RMs determined in the current and previous studies

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf ^a	2s	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf ^a	2s	n ^b
GFZ D ^{g,h}	-0.14	0.10	0.02	-0.08	0.06	0.01	6
Arithmetic mean	-0.15	0.03	0.06	-0.08	0.02	0.03	N^c = 6
NIST SRM 1515 (apple leaves)							
Bristol/UCL	-1.24	0.01	0.01	-0.64	0.08	0.06	3
CGS	-1.24	0.08	0.13	-0.65	0.08	0.13	5
GFZ A (MW) ^{g,h}	-1.24	0.04	0.01	-0.64	0.04	0.01	2
GFZ B ^{g,h}	-1.20	0.04	0.12	-0.61	0.02	0.07	12
GFZ C ^{g,h}	-1.20	0.02	0.02	-0.60	0.08	0.07	3
GEOMAR	-1.19	0.05	0.04	-0.58	0.03	0.03	3
Arithmetic mean	-1.22	0.03	0.05	-0.62	0.03	0.05	N^c = 6
Carbonates							
JDo-1 (dolomite)							
Bristol/UCL	-2.25	0.06	0.05	-1.16	0.05	0.04	3
CGS	-2.49	0.03	0.05	-1.30	0.06	0.12	6
GSI	-2.19	0.04	0.07	-1.14	0.04	0.07	5
GFZ A ^g	-2.36	0.25	0.06	-1.24	0.03	0.01	2
GFZ B ^g	-2.32	0.05	0.10	-1.20	0.03	0.05	6
Wombacher <i>et al.</i> (2009)	-2.38	0.06	0.18	-1.22	0.02	0.07	12
Pearce <i>et al.</i> (2012)	-2.33	0.04	0.09	-1.22	0.025	0.06	7
Mavromatis <i>et al.</i> (2013)	-2.37	0.03	0.08	-1.25	0.02	0.06	9
Mavromatis <i>et al.</i> (2014)	-2.36	0.03	0.06	-1.25	0.03	0.06	6
Beinlich <i>et al.</i> (2014)	-2.38	0.04	0.08	-1.23	0.03	0.05	6
Lavoie <i>et al.</i> (2014)	-2.38	0.29	0.36	-1.27	0.07	0.09	4
Arithmetic mean	-2.35	0.05	0.15	-1.23	0.03	0.09	N^c = 11
BCS-CRM 512 (dolomite)							
Bristol/UCL A ^g	-1.92	0.03	0.02	-1.00	0.02	0.02	3
Bristol/UCL B ^g	-2.01	0.06	0.05	-1.06	0.004	0.003	3
CGS	-2.16	0.11	0.09	-1.13	0.04	0.03	3
GSI	-2.00	0.21	0.27	-1.03	0.09	0.12	4
GFZ A ^g	-2.09	0.29	0.07	-1.08	0.06	0.01	2
GFZ B ^g	-1.97	0.02	0.03	-1.03	0.01	0.02	7
Arithmetic mean	-2.03	0.09	0.17	-1.05	0.05	0.09	N^c = 6
BCS-CRM 513a (limestone)							
Bristol/UCL A ^g	-4.48	0.10	0.08	-2.33	0.07	0.06	3
Bristol/UCL B ^g	-4.50	0.11	0.09	-2.33	0.07	0.06	3
GFZ	-4.41	0.08	0.07	-2.29	0.07	0.06	3
Arithmetic mean	-4.46	0.12	0.10	-2.32	0.05	0.04	N^c = 3

^a 95% confidence intervals calculated as $2SE$ (95% conf) = $t \cdot s/\sqrt{n}$, with s = standard deviation of n (or N) repeated measurements or replicates, t = correction factor for low n (or N) from Student's t -distribution at 95% probability.

^b n is the number of δ values used for the calculation of the result given by each laboratory. As mentioned in Table 2, $n = 1$ refers to one bracket measured at Bristol/UCL, GSI and GFZ, an average of three brackets measured at CGS or an average of nine brackets measured at GEOMAR.

^c N refers to the number of average δ values used for the calculations of the inter-laboratory arithmetic mean.

^d From Pogge von Strandmann *et al.* (2011).

^e Processed through columns.

^f From Foster *et al.* (2010).

^g A, B, C, D and E are replicates of the full procedure including sample dissolution (solids) or evaporation (liquids), Mg column purification and MC-ICP-MS measurements. MW indicates solid sample dissolution using a microwave system.

^h From Uhlig *et al.* (2017).

ⁱ Different samples of the Dead Sea brine.

($\delta^{26}\text{Mg} = -0.67 \pm 0.11\text{‰}$, $\delta^{25}\text{Mg} = -0.35 \pm 0.05\text{‰}$, 2s, $n = 35$, Table 3). Accordingly, our long-term estimate of the typical intermediate precision is $\pm 0.11\text{‰}$ (2s) on $\delta^{26}\text{Mg}$, and $\pm 0.05\text{‰}$ (2s) on $\delta^{25}\text{Mg}$. The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

Sample preparation and Mg isotope ratio measurements at GFZ: Solid powders (30–100 mg) were digested in HF/HNO₃ mixture at 110 °C, followed by 6 mol l⁻¹ HCl, and 14 mol l⁻¹ HNO₃. For all samples, H₂O₂/HNO₃ treatment in closed PFA vials on a hot plate at 150 °C for 24 h was used to remove organics. In addition, a separate

batch of the organic-rich soil (NIST SRM 2709a) and vegetation (NIST SRM 1515) (ca. 1 g) were also acid-digested ($\text{H}_2\text{O}_2/\text{HNO}_3$) using a microwave system (MLS Start) at 160 °C (for 20 min) and elevated pressure. Both the PFA vial-hot plate and the microwave method achieved complete sample dissolution. Water RMs were evaporated on a hot plate (10 to 20 ml for SLRS-5 and NIST SRM 1640a; 0.1 to 0.5 ml for the others), then treated with HF and $\text{H}_2\text{O}_2/\text{HNO}_3$ and evaporated again to remove Si and dissolved organic carbon, respectively. All samples were finally redissolved in 1 mol l⁻¹ HNO_3 , and aliquots containing between 2.5 and 15 µg Mg were taken for Mg purification.

Procedures for Mg purification and isotope ratio measurements are similar to those described previously (Uhlir *et al.* 2017). A brief description of the method applied during this study is given below. Magnesium purification was performed using chromatography columns (Spectrum PP 104704, ID 8 mm) filled with 2.8 ml Bio-Rad AG® 50W-X12 resin. After matrix elution with 32 ml 1 mol l⁻¹ HNO_3 , Mg was quantitatively eluted with 10 ml 2 mol l⁻¹ HNO_3 . The Mg fraction was treated again with $\text{H}_2\text{O}_2/\text{HNO}_3$, evaporated and redissolved in 0.3 mol l⁻¹ HNO_3 . Each material was processed twice through the column procedure. Each column batch was accompanied by at least one commonly used reference material (IAPSO Atlantic seawater, basalts BCR-2, BHVO-2 or granite GS-N) and a blank. Total procedural blanks of the column chemistry and the $\text{H}_2\text{O}_2/\text{HNO}_3$ treatment contained < 12 ng Mg, which is < 0.5% Mg compared with the amount of Mg processed through column chemistry and is therefore considered insignificant (potential bias in $\delta^{26}\text{Mg}$ is estimated < 0.03‰). Magnesium recovery (quantitative column yield), purity of the Mg solutions (> 90% Mg was found to produce no bias using our measurement instrumental set-up; see Pokharel *et al.* 2017) and the Mg content in total procedural blanks were checked by ICP-OES (Varian 720ES) and quadrupole ICP-MS (Thermo Scientific iCAP-Qc), respectively.

Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-MS equipped with a Neptune Plus Jet Interface (using a Pfeiffer OnToolBooster interface pump; standard sample cone and X skimmer cone). The 500 ng ml⁻¹ Mg solutions were introduced into the mass spectrometer via a quartz-glass spray chamber (double pass cyclone-Scott type, Thermo SIS) equipped with a self-aspirating PFA nebuliser with an uptake rate of ca. 100 µl min⁻¹. The ion beam intensities at m/z 24, 25 and 26 were measured simultaneously in medium mass resolution mode (see footnote Table 2) on Faraday detectors (L2, C, H2, all 10¹¹ Ω amplifiers). The H2 cup was slightly

moved towards higher masses so that $^{26}\text{Mg}^+$ was measured on the interference-free low mass side of the flat-top peak (to avoid potential interference from $^{12}\text{C}^{14}\text{N}^+$). $^{27}\text{Al}^+$ and $^{23}\text{Na}^+$ were simultaneously monitored on Faraday detectors H4 and L4, respectively. Each measurement run comprises twenty cycles, with an integration time of 4.2 s for each cycle. These conditions gave sample signal intensities > 10 V for ^{24}Mg . Background intensities (typically < 8 mV ^{24}Mg) were measured on-peak in 0.3 mol l⁻¹ HNO_3 before and after each calibrator-sample bracketing block and were subtracted from the sample and the calibrator signal intensities. Measurement results were accepted only if the instrumental mass bias was stable, that is linear drift < 0.2‰, which is the deviation in $^{26}\text{Mg}/^{24}\text{Mg}$ between two bracketing DSM3 calibrators.

The intermediate precision of this measurement procedure (including dissolution, Mg column separation, dilution and MC-ICP-MS analyses) was evaluated by repeat analyses of reference materials (silicate rocks, IAPSO Atlantic seawater) over the course of about 3 years (e.g., Pokharel *et al.* 2017, Uhlir *et al.* 2017). For example, for BHVO-2 basalt we obtained a mean $\delta^{26}\text{Mg}$ of $-0.24 \pm 0.10\text{‰}$ and a mean $\delta^{25}\text{Mg}$ of $-0.13 \pm 0.06\text{‰}$ (2s, $n = 24$ measurements on $N = 6$ full dissolution and column chemistry replicates), which is identical within stated precisions to results produced independently in other laboratories ($\delta^{26}\text{Mg} = -0.24 \pm 0.08\text{‰}$, $\delta^{25}\text{Mg} = -0.12 \pm 0.05\text{‰}$, Teng 2017 and references therein). Measurements of the pure Mg solution Cambridge-1 (without processing through columns) gave a mean of $-2.61 \pm 0.07\text{‰}$ for $\delta^{26}\text{Mg}$ and $-1.35 \pm 0.05\text{‰}$ for $\delta^{25}\text{Mg}$ (2s, $n = 62$) and IAPSO Atlantic seawater results were $-0.81 \pm 0.12\text{‰}$ for $\delta^{26}\text{Mg}$ and $-0.41 \pm 0.06\text{‰}$ for $\delta^{25}\text{Mg}$ (2s, $n = 13$). Hence, our long-term estimate of the typical intermediate precision (based on repeated analyses on different materials over ca. 3 years) is $\pm 0.10\text{‰}$ (2s) for $\delta^{25}\text{Mg}$ and $\pm 0.06\text{‰}$ (2s) for $\delta^{26}\text{Mg}$, respectively. The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

Sample preparation and Mg isotope ratio measurements at CGS and GEOMAR: Sample preparation for the measurements conducted at CGS and GEOMAR was done in the CGS laboratory according to the following procedure. Carbonate powders were digested in 6 mol l⁻¹ HCl. Powders of the soil NIST SRM 2709a and apple leaves NIST SRM 1515a were successively dissolved in concentrated 1:1 HF:HNO₃ and H₂O₂:HNO₃, respectively, to breakdown the silicate fractions and organic matter. Aliquots of water RMs (equivalent to ca. 20 µg of Mg) were evaporated to dryness and treated with concentrated

HNO₃. Solutions with visible solid residues were once again redissolved in concentrated 1:1 HNO₃:H₂O₂. All sample solutions were then evaporated to dryness and redissolved in 3% v/v HNO₃. Prior to loading samples onto microcolumns, at least 20 µg Mg aliquots were taken, evaporated to dryness and redissolved in 100 µl of 2.5 mol l⁻¹ HCl.

Purification of Mg was accomplished by a three-step chromatographic separation, using 1.25 ml resin (Bio-Rad AG® 50W-X12, 200–400 mesh) in Savillex PFA 3.2 mm × 20 cm (inner diameter × length) microcolumns, for the first and third steps, and 0.12 ml resin in 2.4 mm × 1.5 cm microcolumns for the second step. In the first step, the Mg fraction, which still contains Na and Fe, was separated from other matrix elements by elution with 4.90 ml 2.5 mol l⁻¹ HCl and collected subsequently. In the second step, the Mg fraction (with Fe) was separated from Na by elution with 4.96 ml 0.4 mol l⁻¹ HCl and subsequently collected with 1.5 ml 6 mol l⁻¹ HCl. In the third step, the Mg fraction was separated from Fe by rinsing with 5.2 ml 2 mol l⁻¹ HNO₃ prior to the elution of the purified Mg solution with 5.5 ml 2 mol l⁻¹ HNO₃. The purified Mg fractions were then evaporated to dryness, redissolved in 200 µl concentrated 1:1 HF:HNO₃, evaporated to dryness, redissolved in 200 µl concentrated 1:1 H₂O₂:HNO₃, evaporated to dryness again and finally dissolved in ca. 3% v/v HNO₃ for Mg isotope amount ratios analyses. Total procedural blank was < 2 ng Mg. Mg yields of close to 100% and molar ratios of Σc(matrix cations)/c(Mg) in the final Mg fractions of < 5% were verified by a Thermo Scientific iCAP-Q ICP-MS, as well as a Varian 720 series ICP-OES for each sample.

- Mg isotope ratio measurements at CGS. Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-MS, equipped with Ni sampler and X-Version Ni skimmer cones. The 500 ng ml⁻¹ Mg solutions were introduced into the plasma via a 100 µl min⁻¹ PFA nebuliser and a cyclonic quartz-glass spray chamber. All measurements were carried out with the guard electrode turned on and in medium mass resolution mode (see footnote Table 2). The following cup configuration was used: the ion beam intensities at *m/z* 24, 25 and 26 were measured simultaneously using Faraday cups L1, C and H2, respectively. Measurements were carried out on the low mass side of the peak to avoid ¹²C¹⁴N⁺ interference signals on *m/z* 26. Each individual measurement comprised thirty cycles with 8.4 s acquisition time per cycle. Each single delta value (equivalent to *n* = 1, as reported in Table 3) was calculated by at least three

repeated measurements of the same sample solution, each bracketed by DSM3. Thus, each single delta value reported in Table 3 (*n* = 1) represents an average of three measurements of a sample and four measurements of DSM3. Typical signals on *m/z* 24 were about 4 to 8 V (i.e., ion beam of ²⁴Mg⁺). Procedural blank contributions, including background, were consistently below 0.1% of sample signals. Due to these very low blank contributions to the analyte signals, no on-peak blank corrections were applied. Only an electronic background was collected at half mass unit before each block and subtracted from the measured signals.

Isotope fractionation during column chemistry was not detected with δ²⁶Mg values of -0.01 ± 0.05‰ (2s, *n* = 3, based on a comparison of column processed and unprocessed DSM3), which further substantiates high Mg yields after column chemistry of close to 100%. Measurements of the pure Mg solution Cambridge-1 (without processing through columns) gave a mean of -2.59 ± 0.16‰ for δ²⁶Mg and -1.34 ± 0.11‰ for δ²⁵Mg (2s, *n* = 18). The intermediate precision of the sample preparation procedure and MC-ICP-MS measurement was estimated based on repeat column purifications and measurements of IAPSO Atlantic seawater and was -0.87 ± 0.10‰ for δ²⁶Mg and -0.45 ± 0.06‰ for δ²⁵Mg (2s, *n* = 14) during the period between the years 2012 and 2016. Hence, based on these long-term observations we estimate our typical intermediate precision at ±0.13‰ for δ²⁶Mg and ±0.09‰ for δ²⁵Mg (2s). The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

- Mg isotope ratio measurements at GEOMAR. The magnesium isotope ratio measurements were carried out in August 2012 using a Thermo Scientific AXIOM MC-ICP-MS. RA. Chilton cones (RAC19 and RAC705) were used to achieve the best sensitivity. Samples, prepared as 200 ng ml⁻¹ Mg solutions in 5% v/v HNO₃, were introduced via an ESI MicroFlow PFA-50 nebuliser (50 µl min⁻¹) coupled to a CETAC ARIDUS desolvator (sweep Ar gas: ca. 2 l/min, N₂: ca. 20 ml min⁻¹). Three Faraday cups were utilised (L4: *m/z* 24, AX: *m/z* 25, H4: *m/z* 26) for simultaneous data acquisition. The instrumentation was allowed to stabilise by running for ca. 1 day for preliminary tuning before final fine tuning began. Tuning focused on hot and stable plasma conditions, not primarily on maximum intensity. Typically, 200 ng ml⁻¹ Mg solutions yielded ca. 3.5 V ²⁴Mg⁺ intensity. Each individual measurement result consisted of ten DSM3 calibrator runs bracketing nine runs of the

unknown sample. A single run started with a 15 s on-peak-zero baseline measurement, while clean 5% v/v HNO₃ was introduced, followed by 50 × 2 s data collection (on either reference material or unknown). Finally, sample washout was performed introducing clean 5% v/v HNO₃ for 60 s. Within each run, the collected fifty individual ratios of ²⁵Mg/²⁴Mg and ²⁶Mg/²⁴Mg, respectively, were calculated based on the on-peak baseline-corrected *m/z* 24, 25 and 26 signal intensities. Results were calculated using the mean of the individual ratios after removing statistical outliers (1s). Each run of the unknown was used to calculate the δ -value relative to the preceding and following runs of DSM3. The resulting nine δ -values were combined to an average for the measurement. Each measurement consumed about 200 ng of total Mg.

The repeatability precision is estimated by repeated measurements of Cambridge-1 during this study (without processing through columns), which gave $-2.58 \pm 0.08\text{‰}$ for $\delta^{26}\text{Mg}$ and $-1.33 \pm 0.06\text{‰}$ for $\delta^{25}\text{Mg}$ (2s, *n* = 11). Measurements of Cambridge-1 processed through columns gave $-2.63 \pm 0.12\text{‰}$ for $\delta^{26}\text{Mg}$ and $-1.31 \pm 0.03\text{‰}$ for $\delta^{25}\text{Mg}$ (2s, *n* = 3; Table 3). The results agree with data obtained in other laboratories, indicating no bias outside the stated precision. Because no long-term data on repeated measurements on materials with different matrices are available to estimate the typical intermediate precision of the GEOMAR laboratory, as was done for the other laboratories, the typical precision was estimated by the long-term repeatability of the MC-ICP-MS to be $\pm 0.08\text{‰}$ (2s) for $\delta^{26}\text{Mg}$ and $\pm 0.06\text{‰}$ (2s) for $\delta^{25}\text{Mg}$, based on the unprocessed Cambridge-1 results.

Results and discussion

Individual results validation of the participating laboratories

All the $\delta^{26}\text{Mg}'$ versus $\delta^{25}\text{Mg}'$ results determined in different laboratories during this study plot on a single line with a slope of 0.518 ± 0.004 (Figure 1; linear fit was obtained using the *Isoplot* software), suggesting no major influence of isobaric interferences on the measured Mg isotope ratios. In addition, the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of Cambridge-1 and seawater, on which large data sets are available in the literature (e.g., compilations in Foster *et al.* 2010, Pogge von Strandmann *et al.* 2011, Ling *et al.* 2011, An and Huang 2014, Teng 2017, and references therein and in the GeoReM database, Jochum *et al.* 2005), were used to validate the individual measurement procedures

and measurement results performed by each laboratory. First, to validate each mass spectrometric measurement procedure, the pure Mg solution Cambridge-1 was analysed without processing through Mg column chemistry. Second, to include the various sample preparation methods for Mg purification in the interlaboratory comparison, IAPSO Atlantic seawater, which contains a complex element matrix ($\Sigma c(\text{matrix cations})/c(\text{Mg}) = 9.2$; Table 1), was processed and analysed repeatedly in each laboratory. For both RMs, the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values agree well between all laboratories. The absolute differences (bias) between the values measured in this study and published consensus values are less than 0.04‰ and 0.03‰ for $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$, respectively (Table 3, Figure 2), which are well within the precisions reported by each laboratory. These observations indicate that the various measurement procedures (including sample preparation and MC-ICP-MS measurements) do not induce any significant bias outside the reported measurement precision. However, due to the fact that all measurements in this and previous studies were conducted by MC-ICP-MS instruments, an independent validation using a different method cannot be made to exclude any potential systematic MC-ICP-MS bias. However, to date no other technique is able to measure $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ at the level of precision obtainable by MC-ICP-MS.

The MC-ICP-MS repeatability precision for Cambridge-1 determined by each laboratory ranges from 0.07 to 0.16‰ (2s) for $\delta^{26}\text{Mg}$ and 0.03 to 0.11‰ (2s) for $\delta^{25}\text{Mg}$ (Table 3). The intermediate precision of the entire measurement procedure based on multiple IAPSO Atlantic seawater sample preparations and MC-ICP-MS analyses ranges from 0.04 to 0.12‰ (2s) for $\delta^{26}\text{Mg}$ and 0.04 to 0.09‰ (2s) for $\delta^{25}\text{Mg}$ (Table 3). Because the 2s of IAPSO Atlantic seawater results is not systematically larger than the precision (2s) of Cambridge-1 results, we conclude that the different sample preparation methods do not introduce any additional significant sources of uncertainty that are not already included in the intermediate measurement precision (2s) reported for each RM result by the different laboratories.

These findings are also consistent with the 'typical' intermediate precision reported by each laboratory, based on $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values measurements of various RMs and natural samples over the long term (between 0.06‰ and 0.13‰, 2s, in $\delta^{26}\text{Mg}$, and 0.04‰ and 0.09‰, 2s, in $\delta^{25}\text{Mg}$, Table 2, Figure 2). Thus, the individual results from the different laboratories can be used to evaluate the consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of the 'new' Earth-surface RMs analysed in this study. This means that the consensus mean $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of the full-procedure replicates measured by the different laboratories

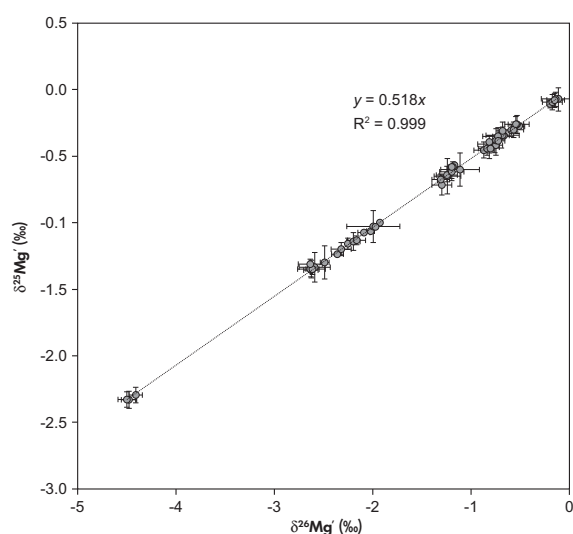


Figure 1. $\delta^{25}\text{Mg}'$ versus $\delta^{26}\text{Mg}'$ values determined in this study. Error bars are 2s of each result. The data are in accordance with a regression line (dotted) that crosses the origin and has a slope of 0.52, typical of mass-dependent fractionation of terrestrial material.

and their variance (reported both as 2s and 95% confidence interval in Tables 3 and 4) include random errors that stem from all influencing factors (sample preparation, matrix separation, instrumental conditions, etc.). Hence, following a 'top-down' approach of uncertainty evaluation (e.g., Potts 2012a, b), we report consensus mean values for each Earth-surface RM characterised in this study together with an uncertainty statement (95% confidence interval, based on the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values reported by each laboratory, as discussed in the next section.

Assigning consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values to the reference materials

The results of the eight RMs, from the laboratories participating in this study, as well as the available literature data, are shown in Table 3 and Figure 2. The range of $\delta^{26}\text{Mg}$ values of the studied RMs covers almost the entire range of terrestrial materials (e.g., Teng 2017). As expected, the lowest $\delta^{26}\text{Mg}$ values were found in carbonates: limestone BCS-CRM 513a ($-4.46 \pm 0.12\text{‰}$, 95% conf., $n = 3$), which represents the lower part of the global $\delta^{26}\text{Mg}$ range of limestones, and dolomites JDo-1 and BCS-CRM 512 ($-2.35 \pm 0.05\text{‰}$, 95% conf., $n = 11$ and $-2.03 \pm 0.09\text{‰}$, 95% conf., $n = 6$, respectively), which are within the typical range for dolomites (Teng 2017 and references therein). The most positive $\delta^{26}\text{Mg}$ value was found in the soil NIST SRM 2709a ($-0.15 \pm 0.03\text{‰}$, 95% conf., $n = 6$), typical for silicate soils (Teng 2017 and references therein).

NIST SRM 1515 (apple leaves) has $\delta^{26}\text{Mg}$ value of $-1.22 \pm 0.03\text{‰}$ (95% conf., $n = 6$), consistent with previous findings. $\delta^{26}\text{Mg}$ values in plants depend on the sources of Mg and on complex isotope fractionation processes during the uptake of Mg and transport within the plant (e.g., Black *et al.* 2008, Bolou-Bi *et al.* 2010, 2012, Tipper *et al.* 2010). In general, Mg in rivers and groundwater yield a large range of $\delta^{26}\text{Mg}$ values with a flux-weighted $\delta^{26}\text{Mg}$ of global run-off of -1.09‰ (Tipper *et al.* 2006b). SLRS-5 river water ($-1.22 \pm 0.06\text{‰}$, 95% conf., $n = 8$) has lower $\delta^{26}\text{Mg}$ value, and spring water NIST SRM 1640a ($-0.73 \pm 0.03\text{‰}$, 95% conf., $n = 9$) has higher $\delta^{26}\text{Mg}$ value, relative to this average. The higher $\delta^{26}\text{Mg}$ value of the Dead Sea brine (DSW-1; $-0.58 \pm 0.05\text{‰}$, 95% conf., $n = 8$) relative to its precursor seawater may represent a contribution of ^{24}Mg -depleted dolomitising brines (Gavrieli *et al.* 2009, Shalev *et al.* 2014).

To obtain mean $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for the RMs, we evaluate the interlaboratory reproducibility (indicated as 2s on the consensus value derived from the results of all laboratories and literature data; Table 3). All eight RMs have an interlaboratory reproducibility (2s) of 0.05 to 0.17‰ in $\delta^{26}\text{Mg}$. For most RMs (DSW-1, NIST SRM 1640a, NIST SRM 2709a, NIST SRM 1515 and BCS-CRM 513), the interlaboratory reproducibility ($0.05\text{--}0.12\text{‰}$) is within or below the range of the 'typical' intermediate precision of the laboratories estimated from repeat analysis of different materials over the long term ($0.06\text{--}0.13\text{‰}$ in $\delta^{26}\text{Mg}$), indicating that the measurement procedures used in all laboratories do not induce any additional uncertainty contributions when samples with such matrices are processed and measured. For these RMs, the individual results from all laboratories also agree within the reported measurement precision of each sample (Table 3 and Figure 2). However, the interlaboratory reproducibilities of three RMs, river water SLRS-5, dolomites JDo-1 and BCS-CRM 512 (2s of 0.15‰ , 0.15‰ and 0.17‰ , respectively), are slightly higher than the 'typical' intermediate precisions reported by the participating laboratories. While all the individual SLRS-5 results agree within 2s measurement precision of the repeat measurements of each RM, this is not the case for all individual results of JDo-1 and BCS-CRM 512 (Figure 2). Averaged data of JDo-1 reported in the literature seem to be more uniform, but in some cases, the reported 2s is larger, covering the whole range obtained in current research (Wombacher *et al.* 2009, Pearce *et al.* 2012, Mavromatis *et al.* 2013, 2014, Beinlich *et al.* 2014, Lavoie *et al.* 2014, Figure 2). Similar to the results of this study, Wombacher *et al.* (2009) reported a precision of 0.18‰ (2s) on the mean of twelve measurement results of JDo-1 from four different Mg separations (test portions of 2.5–40 mg). Note that most of these values (Pearce *et al.* 2012,

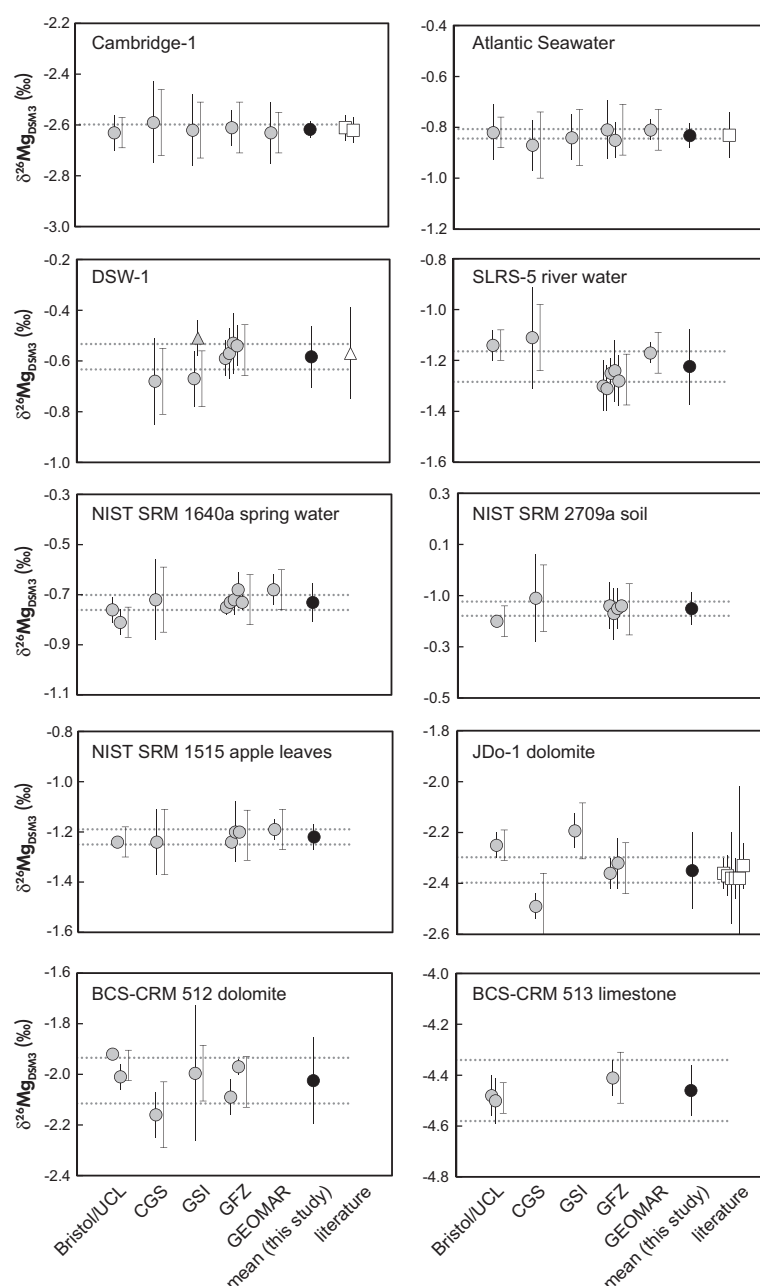


Figure 2. $\delta^{26}\text{Mg}$ values of the studied Earth-surface low-temperature materials. Individual results from each laboratory (grey circles) are presented with their repeatability precision ($2s$, twice the standard deviation of n repeated measurements). Multiple results from individual laboratories represent full-procedure replicates (including dissolution, Mg columns and MC-ICP-MS measurements). Capped error bars next to each individual results indicate the typical intermediate precision ($2s$) for each laboratory (based on repeat analyses of samples with different matrices over the long-term) for comparison with the measurement precision of the matrix RMs. Available literature data (specified in Table 3) are also presented (white squares). Triangles, in the DSW-1 plot, refer to different samples of the Dead Sea brine. The interlaboratory arithmetic mean of these individual results is also shown (black circle) with $2s$ error bars and 95% confidence interval (presented by grey dotted lines). The vertical axis in all plots ranges 0.8‰.

Mavromatis *et al.* 2013, 2014, Beinlich *et al.* 2014) were obtained using a similar chemical sample preparation procedure.

The reasons for the slightly higher interlaboratory variance in the dolomite RMs are unknown. Interlaboratory variance can arise from many factors, including material

Table 4.

Interlaboratory consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values from this study and literature, if available, of low-temperature, Earth-surface reference materials

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf ^a	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf ^a	N ^b
DSW-1 (Dead Sea brine)	-0.58	0.05	-0.30	0.03	8
SLRS-5 (river water)	-1.22	0.06	-0.64	0.04	8
NIST SRM 1640a (spring water)	-0.73	0.03	-0.38	0.03	9
NIST SRM 2709a (soil)	-0.15	0.03	-0.08	0.02	6
NIST SRM 1515 (apple leaves)	-1.22	0.03	-0.62	0.03	6
JDo-1 (dolomite)	-2.35	0.05	-1.23	0.03	11
BCS-CRM 512 (dolomite)	-2.03	0.09	-1.05	0.05	6
BCS-CRM 513a (limestone)	-4.46	0.12	-2.32	0.05	3

^a 95% confidence intervals calculated as $2SE$, (95% conf) = $t \cdot s / \sqrt{N}$, with s = standard deviation of N full-procedure replicates, t = correction factor for low N from Student's t -distribution at 95% probability.

^b N is the number of results used for the calculation of the consensus values and the 95% confidence interval. These are detailed in Table 3.

properties (e.g., homogeneity at the level of the test portion, or stability over time), sample preparation procedure (e.g., incomplete dissolution, column yield, analyte purity and blank) and the procedures used in the mass spectrometric measurements and data reduction (e.g., mass bias stability and mass bias correction, matrix effects). No correlation was found between molar matrix elements/Mg ratios and the interlaboratory variance (examples in Figure 3). Moreover,

we checked for any correlations between individual $\delta^{26}\text{Mg}$ values and test portions, blank/Mg, column capacity, but did not find any systematic relations. Thus, further investigation on these RMs is required to determine the sources of the observed variance.

The consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ mean values for the studied RMs are provided in Table 4 together with an

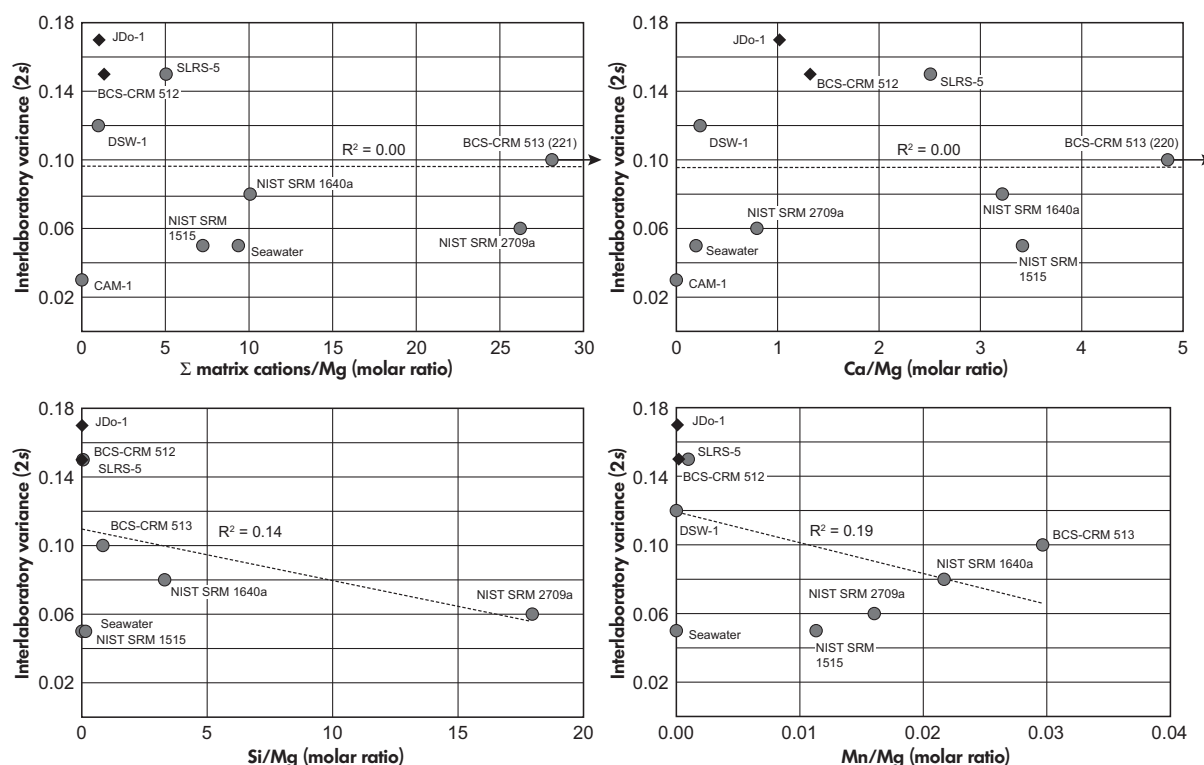


Figure 3. Interlaboratory variance ($2s$ reproducibilities) of the studied materials versus selected matrix element molar ratios (before Mg purification by column chemistry). Dolomite RMs (JDo-1, BCS-CRM 512), are shown as diamonds. Low R^2 of the linear regression lines (dashed lines) demonstrates absence of any correlation.

associated uncertainty for each value. This uncertainty was estimated by the 95% confidence interval on the mean of *N* laboratory results, including literature data, if available.

Summary and conclusions

In this study, the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of eight Earth-surface reference materials (RMs), representative of different low-temperature environments and material types were determined by interlaboratory comparison. Despite the differences in sample preparation procedures, different test portions, instrumentation and isotope ratio measurement procedures, good agreement of the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ data from the different laboratories was found. This encouraging result suggests that all methods described in this study are suitable for geochemical studies on these types of materials given they are strictly monitored and calibrated (recovery, blanks, matrix removal, etc.). Moreover, the investigated RMs are suitable to be used by other laboratories for routine quality control of Mg isotope ratio measurement procedures during environmental and Earth-surface geochemical studies. The wide range of matrices, including river water, spring water, brine, dolomites, limestone, soil and plant leaves, allow analysts to identify potential issues (and facilitate modifications) with sample preparation methods previously developed for silicate rocks, for example, which are then applied to different sample types, such as Ca-rich carbonates, organic-rich soils or vegetation.

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